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Published in:
Proceedings of the 22nd world congress & exhibition

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

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Effect of ozonation on THM formation in swimming pool water – laboratory study

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Abstract

Ozonation experiments were performed with pool filling water (drinking water; unchlorinated groundwater), pool water and pool water mixed with filling water and artificial body fluid to evaluate the effect of ozonation on total trihalomethane (TTHM) formation during subsequent chlorination.
The lifetime of ozone followed first order kinetic and in the filling water the half-lifetime was 4 min while for the mixture and the pool water it was 8 and 11 min, respectively. When the ozonated was repeated the half-lifetime of ozone increased to 17-19 min in all samples.
The subsequent chlorination revealed that ozone removed reactivity of the dissolved organic carbon toward chlorine for the filling water and the mixed water samples and decreased TTHM formation. For the pool water samples, a higher TTHM formation was observed in ozonated than non-ozonated water. Thus, in the filling water and the mixed water samples ozone reacted directly with the pollutants resulting in short lifetimes of ozone and removed reactivity of the pollutants towards chlorine oxidation and prevented TTHM production. Whereas in the pool water samples, due to the long lifetime ozone decomposed to hydroxyl radicals, which then reacted with the pollutants and increased the chlorine reactivity of the pollutants.
Thus, it was observed that ozone reacted markedly different in swimming pool water than in drinking water. Therefore, ozonation in pool water should be designed such that ozone mostly react with fresh pollutants from bathers and filling water before chlorine has time to oxidise it, since ozonation of aged pool water might increase TTHM production in short term.

Key-words: Ozone, swimming pool, trihalomethane.

Introduction

Chlorine is the most common disinfectant for public swimming pools. However, chlorine reacts with pollutants introduced into the water by bathers and forms disinfection by-products (DBPs). Actually, the main removal processes of the dissolved organic pollutant are oxidation and mineralization through oxidation by chlorine. Ozone is a strong oxidizing agent, which if applied to swimming pool water could oxidize the dissolved pollutants (Dissolved organic carbon (DOC); Eq. 1) and reduce their ability to form disinfection by-products (DBPs) with chlorine. In a Korean study, ozone/chlorine treated swimming pools had lower levels of DBPs than chlorinated pools [1].

$$DOC + O_3 \rightarrow DOC_{ox} \quad \text{Eq. 1}$$
$$H_2O + O_3 \rightarrow O_2 + 2\,HO^{\bullet} \quad (HO^- \text{ catalysed}) \quad \text{Eq. 2}$$
$$DOC + HO^{\bullet} \rightarrow DOC_{ox} \quad \text{Eq. 3}$$

The ozone may also decompose to hydroxyl radicals (Eq. 2) and the rate of decomposition increases with increasing pH [2]. Hydroxyl radicals are non-selective and highly reactive and thus they can oxidize the dissolved pollutants (Eq. 3).
Generally, most ozonation treatment of swimming pools is built based on the German DIN standard where all or a part of the water is ozonated with a contact time of 3-10 min before deozonation on an activated carbon filter. The deozonation performed to prevent ozone escaping to the air in the swimming pool, but it results in that only a small part of the ozone reacts with the treatment targets while the main part will be destroyed. A radical different treatment principle, which emerges from USA, is the slip-stream ozonation method which applied a low dose of ozone into a side stream of the filter flow. The low dose of ozone is consumed fast by reaction with organic in the main recirculation flow. The ozone dosing is controlled by a redox probe to ensure

ozone is not added in excess to dissolved organic matter and therefore it is ensured that ozone does not reach the pool.
Literature on effect of ozone on DBP formation in swimming pool water is limited. However, general knowledge about ozone and reactivity can be found in literature on the topic of ozonation of drinking water and wastewater e.g. von Gunten [3], where it is seen that the most common DBPs, THM and HAA react very slowly with ozone. Ozone's reaction with nitrogen compounds and chloramine is also relatively slow [4]. However, in a field application of ozone treatment of swimming pool water according to DIN standard, 34-48 % decrease in chloroform formation potential was achieved depending on ozone contact time [5]. While in laboratory batch experiment, Glauner et al. [6] obtained 12 % reduction of absorbable organohalogen (AOX) formation potential and 3% reduction in total trihalomethane (TTHM) formation potential after 10 min oxidation by ozone.
An increased understanding of ozonation in swimming pools e.g. half-life time could help in making a more cost effective ozone treatment and minimize the occurrence of disinfection by-products in swimming pools. Thus, the aim is to determine the half-life time of ozone in pool water and investigate the effect of ozonation on TTHM formation.

Material and methods

Reagents

All reagents and chemicals were purchased at Sigma-Aldrich (Denmark) and used as received. The experimental set-up for the ozonation was based on a 20 g/h ozone generator from O3-Technology AB (Vellinge, Sweden) which was supplied with dry oxygen gas. The generated ozone was dispersed through a diffuser in a collection bottle containing ultra-pure water, which was immersed in an ice bath so that ozone solubility is increased. To further increase the solubility of the ozone a manometer and a valve were placed after the collection bottle and a pressure at 1.4 barg was established. Based on these experimental conditions, the concentration of ozone in the stock solution was between 80 and 100 mg/L.

Analysis of ozone, TOC, chlorine, hydrogen peroxide

Ozone. Ozone concentration was quantified with the indigo method [7]. The reagents used were 0.5 M phosphate buffer at pH 2 and 1.00 g/L indigo trisulphate dissolved in 20 mM phosphoric acid. For the ozone decomposition profile, the volumes from Bader and Hoigné [7] were downscaled to fit into a 3 mL cuvette. Specifically, 0.100 mL indigo trisulphonate (1.0 g/L) and 0.250 mL phosphate buffer (0.5 M at pH 2) were added to the cuvette. Then ultra-pure water and sample were added so the total volume was 2.5 mL. The amount of sample and ultra-pure water were varied depending on ozone concentration. The absorbance of the unreacted indigo trisulphonate was measured at 600 nm. Comparing the absorbance of a blank with the sample and using ΔA = -20000 1/(cm·mol ozone added per L), the ozone concentration was determined.
The delivered ozone dose was determined by adding sufficient amount of indigo and 10 mL phosphate buffer into 100 mL. For instance, a water sample (100 mL) was ozonated with an ozone dose of 2 mg/L. To determine the delivered ozone dose, 4.0 mL indigo trisulphate (1.0 g/L) and 10 mL phosphate buffer were added in a 100 mL volumetric flask, and then filled to the mark with ultra-pure water and poured into a glass bottle. The same amount of ozone stock solution was then added to the glass bottle as added to the water sample. The absorbance of the unreacted indigo trisulphonate was measured at 600 nm and compared to the absorbance of a blank. The ozone dose was then determined using ΔA = -20000 1/(cm·mol ozone added per L).
Total organic carbon. A Shimadzu ASI-V UVC/Persulphate analyzer was utilized for the quantification of the remaining total organic carbon (TOC) in the samples. Sample injection volume was 3.00 mL and a calibration curve was formed using standards with concentrations ranging from 50-2000 µg/L (R^2 = 0.9994). The method quantification limit is 50 µg/L.
Chlorine. The concentration of chlorine and combined chlorine in the swimming pool samples were quantified at the arrival using DPD based test kit (LCK 310, Hach Lange, Denmark). The concentration of chlorine during experiments was quantified using ABTS method [8].
Hydrogen peroxide. Hydrogen peroxide was analysed by colorimetric method using potassium TiO-oxalate [9].

Experiments

Experiment 1: Repeated ozonation. A water sample was divided into 5 subsamples (300 mL each) and placed in a circulation bath with controlled temperature at 28 °C. Four of the subsamples were ozonated with 2 mg/L ozone. The delivered ozone dose was determined as previously descripted. In one of the subsamples the ozone concentration was measured over time. When the ozone was decomposed, the ozonation was repeated but this time only with the remaining three samples. Again the ozone concentration was determined over time in one of the samples. The samples used for ozone profiles and the non-ozonated sample were subsequently chlorinated. The water samples were transferred to 40 mL glass vials where chlorine and boric acid were added to samples based on chlorine consumption measured by ABTS. Chlorine consumption was determined in pre-experimental tests to have a chlorine residual of 1-3 mg/L after 24 h. After 24 h at 25 °C, residual chlorine was determined and samples analyzed the same day for THM by purge and trap (purge temperature = 30 °C, Velocity XPT Purge and Trap Sample Concentrator, Teledyne Tekmar, with auto-sampler: AQUATek 70, Teledyne Tekmar) coupled with a GC–MS (HP 6890 Series GC System, 5973 Mass selective detector, Hewlett Packard). Detailed description of THM analysis can be found in Hansen et al. [10].

Experiment 2: Fresh material. Pool water was mixed with tap water (20%). Furthermore, it was spiked with an artificial body fluid consistent of main components of sweat and urine [11]. The mixture was then divided into subsamples which were ozonated with different ozone doses ranging from 0.7 mg/L to 3.4 mg/L. A highly ozonated sample was produced by replacing the ultra-pure water in the collection bottle with the pool mixture and let the sample be ozonated for 30 min. The samples were placed at 28 °C for 12 hours before chlorine was added. The residual chlorine after 24 hours at 25 °C was 1.0±0.3 mg/L. Afterwards, the concentration of THMs was determined as described in Hansen et al. [10].

TOC was measured before and after ozonation.

Results and discussion

Repeated ozonation

Ozonation experiments were performed with filling water (unchlorinated groundwater), pool water and pool water mixed with filling water and artificial body fluid. The pool water was collected from a swimming pool in Copenhagen area. Concentration of ozone was measured over time (Figure 1). In the case of filling water, it can be seen that the first dose disappeared faster ($t_{½}$ = 3.8 min) than the second and third ($t_{½,2nd}$ = 19 min and $t_{½,3rd}$ = 17 min). So the first dose reacted with the easily ozonated DOC while at second and third dose the ozone reacted with more slowly reactive DOC or decomposed to hydroxyl radicals. For the pool water, the first ozone dose reacted slower ($t_{½}$ = 11 min) compared to filling water. However, the second dose disappeared faster ($t_{½}$ = 8 min). Due to the long lifetime of the first ozone dose, some of the ozone was decomposed to hydroxyl radicals which reacted with the DOC and made it more reactive towards ozonation during the second dose. The half-lifetime of the third and fourth dose ($t_{½,3rd}$ = 17 min, $t_{½,4th}$ = 18 min) were similar to those (2^{nd} and 3^{rd}) for the filling water. For the mixed water samples, the first ozone dose reacted faster ($t_{½}$ = 8.4 min) than the pool water but slower than the filling water which fits with the fact that the water is a mixture of fresh non-chlorinated pollutants (filling water and artificial body fluids) and less reactive pollutants from the pool water. The half-life time of 2^{nd} and 3^{rd} dose ($t_{½,\ 2^{nd}}$ = 16 min and $t_{½,\ 3rd}$ = 18 min) were quite similar to those for the filling water (2^{nd} and 3^{rd}) and pool water (3^{rd} and 4^{th}). Thus, the first ozone dose reacted with the reactive DOC and then the ozone doses reacted with the more slowly reacting DOC or ozone decomposed to hydroxyl radicals (Eq. 2) which then reacted with the DOC (Eq. 3).

Chlorination of filling water formed a lot of TTHM. After the addition of 2 mg/L of ozone, the formation was decreased 40 % (Figure 2B). However, repeating the ozone treatment did not decrease the THM formation further. The chlorine consumption (Figure 2A) decreased with the first dose and then for the next ozone doses it increased again slowly. A likely explanation is that ozone reacted with the functional groups of NOM which otherwise would react with chlorine resulting in THM formation and thereby a small amount of ozone decreased the formation potential of the filling water. Furthermore, the filling water contains some bromide which when chlorinated ends up as brominated THM. The ozone oxidized bromide to bromate, which will not end up as brominated THM when chlorinated. However, this is not advantageous as bromate is carcinogenic and should be avoided in swimming pools.

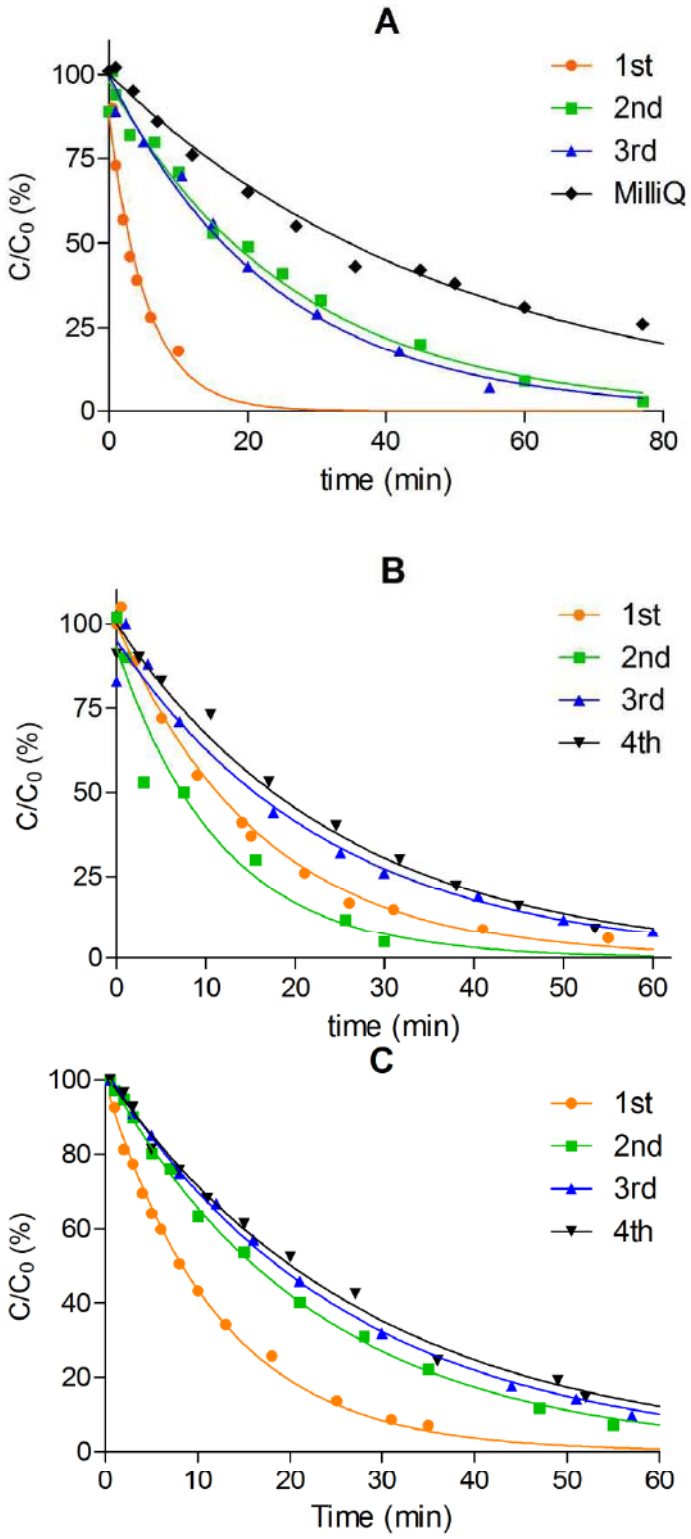

Figure 1. Concentration profile of ozone in A) filling water (pH = 7.9, DOC = 2 mg/L) and MilliQ water (buffered at pH 7.3 with phosphate), B) swimming pool water (pH = 7.3, DOC = 1.5 mg/L), and C) mixture consisting of 80% pool water, 20% tap water and artificial body fluid (pH = 7.3, DOC = 2.4 mg/L). The water samples were treated repeatedly with an ozone dose of approximately 2 mg/L.

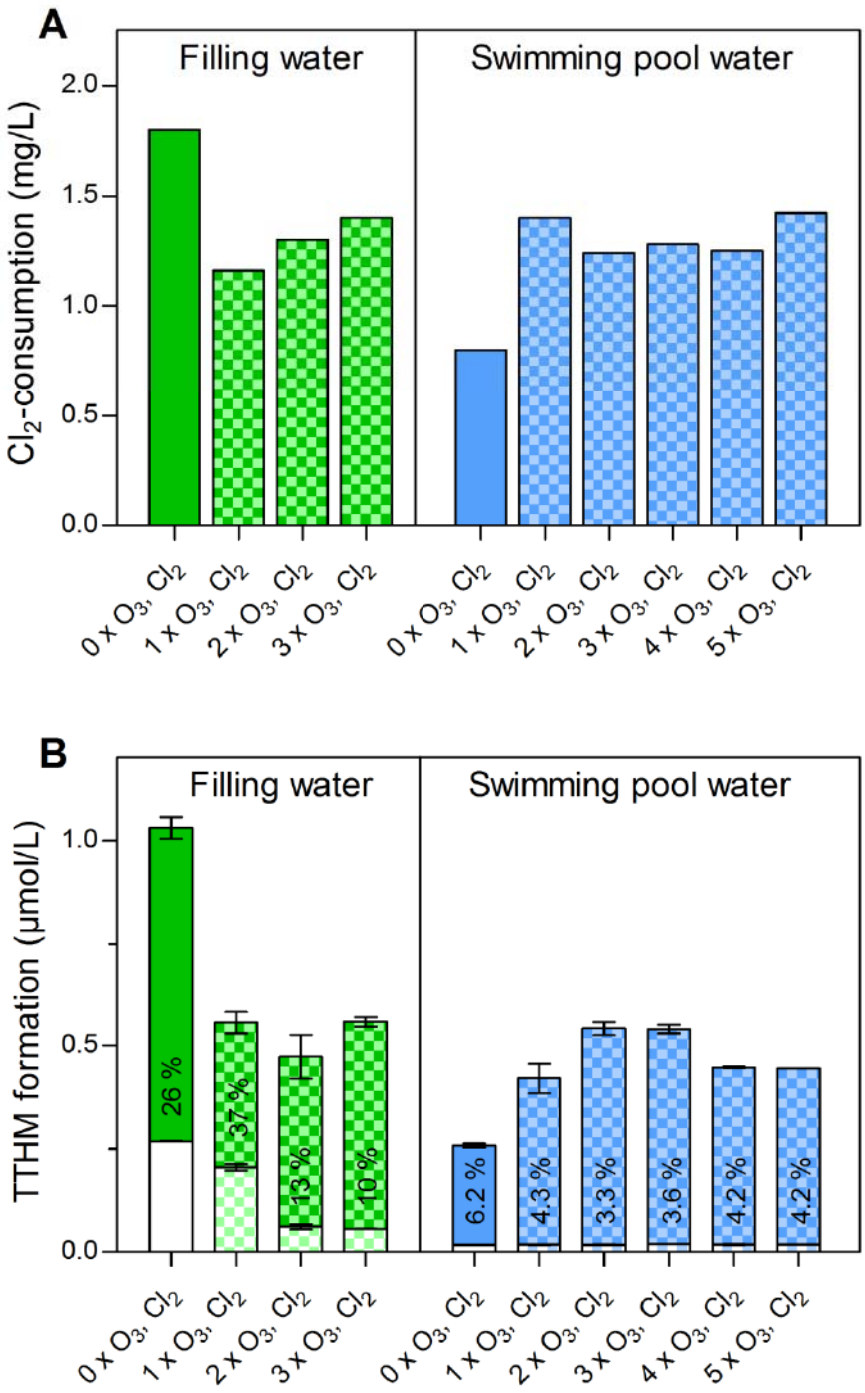

Figure 2. A) The chlorine consumption for filling water and swimming pool water with repeated ozonation. B) The formation of total trihalomethane (TTHM) at repeated ozonation of filling water and swimming pool water. The white part represent the amount of incorporated bromine in TTHM; also given as percentages.

For swimming pool water, firstly an increase in THM formation and then a decrease were observed. Likewise, there was observed an increase for chlorine consumption at the first ozone dose. Nevertheless, for the following ozone doses, the chlorine consumption remained the same. This means that ozone first makes the DOC more reactive towards chlorine and then removes this reactivity again. The amount of bromine in the pool water is low and the bromine incorporation did not change during the experiments.

Fresh material

The addition of tap water and artificial body fluid to the pool water more than doubled the DOC level of the water sample (Figure 3A). The treatment with ozone resulted in a minor decrease in DOC levels for treatment with ozone dose from 0.7 to 3.4. For the high ozonated samples (Mix: [~100 ppm $O3]_{30min}$,Cl_2), which were exposed to approximately 100 mg/L of ozone for 30 min, the

DOC level was decreased to 1/5 of the mixture and actually the DOC level was lower than in the pool water.
The chlorine consumption of pool water was quite low compared to the mixed water sample (Figure 3B). The reason for this is that the pool water had been chlorinated for long time and most of the DOC in the pool water has already been oxidised by chlorine whereas the mixture contained a lot of fresh non-chlorinated DOC which easily reacted with chlorine. Treatment with small amount of ozone decreased the chlorine consumption (Figure 3B, Mix:Cl_2 vs Mix:0.7ppmO_3,Cl_2) while the increase in ozone dose did not lead to further decrease in chlorine consumption expect for the high ozonated sample where chlorine consumption was decreased to almost half of value for the non ozonated mixed water sample.

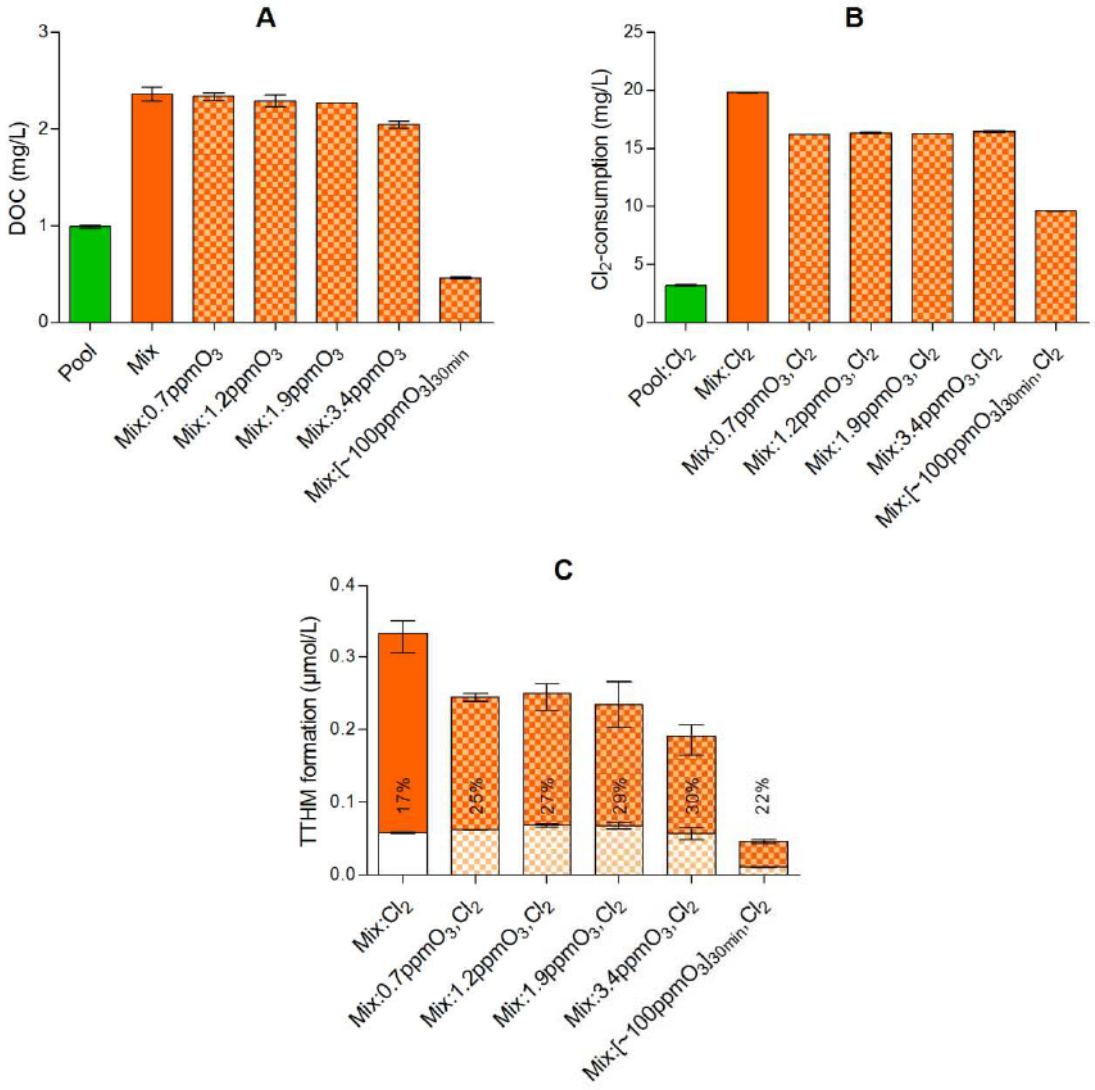

Figure 3. A) DOC level in pool water, mixture and ozonated mixture. B) Chlorine consumption (Temperature = 25 °C, 24 h). C) Total trihalomethane formation after chlorination. The white part represent the amount of incorporated bromine in TTHM; also given as percentages. The error bars indicates minimum and maximum measured values.

The TTHM formation decreased when water sample was treated with 0.7 mg O_3/L prior to chlorination (Figure 3C). A decrease in TTHM formation was observed with increasing ozone dose in the range of 0.7- 3.4 mg/L ozone. The high ozonated samples had the lowest TTHM formation because ozone had mineralized the main part of the DOC.
The decrease in TTHM formation in the ozonated samples fits with the decrease in DOC and chlorine consumption in those samples. Thus ozone is oxidizing the fresh material (Eq. 1) and makes it less reactive towards oxidation by chlorine. The amount of bromine that was incorporated in the TTHM remained unchanged during the treatment with low ozone doses since ozone had

relative short lifetime in the mixed water sample at low ozone doses and therefore, it did not oxidize bromide to bromate. In the high ozonated water sample, the amount of incorporated bromine decreased as ozone oxidized bromide.

Conclusions

The results showed that

- Ozonation of filling water (non-chlorinated ground water) and pool water with fresh non-chlorinated pollution reduced the THM formation
- Ozonation of pool water increased THM formation as ozone react slowly with the organic matter that remains after extended chlorination and thus converts to hydroxyl radicals that reacted with the dissolved organic pollutant making it more reactive to subsequent chlorination.
- High ozone doses decreased the total organic matter by oxidation and the fraction of TTHMs which are brominated. Properly as bromide is completely oxidised to bromate.

Thus, in the design of ozonation of pool water as a water treatment, it is important that ozone is able to react with the fresh pollutants and before chlorine reacts with it.

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